

Chapter 10

Conclusions and Recommendations

10.1 Electric Utility Coal Combustion and Air Pollution Control Technologies

The diversity of coals and combustion technologies used for electrical utility steam generating units (i.e., coal-fired boilers) is reflected in data gathered from Phases I and II of the EPA's formal information collection request (ICR) to the electric utility industry. In 1999, electric utility coal-fired boilers in the United States burned 786 million tons of coal of which about 52 percent was bituminous coal, 37 percent was subbituminous coal, and 9 percent was lignite. Other fuels burned in electric utility coal-fired boilers included mixtures of bituminous and subbituminous coal, mixtures of coal and petroleum coke (pet-coke), reclaimed coal wastes, and mixtures of coal and tire-derived fuel (TDF).

There were 1,140 coal-fired boiler units that burned coal by conventional methods and three units that used gasification to produce a fuel gas. Pulverized-coal-fired (PC) boilers, by far the largest group of coal-fired boiler units, represent approximately 86 percent of the total number of units and 90 percent of the total utility boiler capacity. Based on capacity, other types of boilers include cyclone-fired boilers (7.6 percent), fluidized-bed combustors (1.3 percent), and stoker-fired boilers (1.0 percent).

The Part II EPA ICR responses indicate that a variety of air emission control technologies are employed to meet requirements for control of sulfur dioxide (SO₂), nitrogen oxides (NO_x), and particulate matter (PM). Most utilities control NO_x by combustion modification techniques and control SO₂ by the use of compliance coals. For post-combustion controls, 77.4 percent of units by number have PM control only, 18.6 percent have both PM and SO₂ controls, 2.5 percent have PM and post-combustion NO_x controls, and 1.3 percent have three post-combustion control devices.

For PM emissions control of electric utility coal-fired boilers, electrostatic precipitators (ESPs) are used on 84 percent of the units and fabric filters (FFs) on 14 percent. Post-combustion SO₂ controls are less common. Wet flue gas desulfurization (FGD) scrubbers are used on 15.1 percent of the units, and spray dryer absorbers (SDA) are used on 4.6 percent of the units surveyed. In 1999, while the application of post-combustion NO_x controls was becoming more prevalent, only 3.8 percent of the units used either selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) systems.

10.2 Mercury Measurement Methods

Reliable and valid speciated and total Hg measurements, by either manual test methods or continuous emission monitors (CEMs), are critical to the characterization and future reduction of Hg emissions from coal-fired powered plants. Although viable measurement techniques exist for certain measurement scenarios, acceptable measurement techniques are not available to meet all measurement needs. Additional research and development is needed to enable quality measurements from various measurement environments.

The Ontario-Hydro (OH) Method is the only manual test method that currently is recognized in the United States for the collection of speciated Hg emissions data from the combustion of coal. The OH Method appears to provide valid speciation results at sampling locations downstream of PM control devices where most of the fly ash has been removed. However, measurements made upstream of PM control devices are susceptible to measurement artifacts that bias speciation measurements, causing significant uncertainty in results.

A limited number of CEMs exist (both commercial and prototype) for the measurement of total gas-phase Hg and, to a lesser extent, speciated gas-phase Hg. Also, demonstration of acceptable measurement performance under field applications is limited. Because of the diversity and severity of associated measurement environments, numerous measurement obstacles exist (e.g., PM artifacts, interferences, Hg²⁺ conversion systems, sample conditioning/delivery) that have not been adequately addressed, particularly with respect to speciated measurements. While experts use Hg CEMs as a research tool, the Hg CEMs are not currently suitable for routine use on power plants in the United States.

Improved methods for the sampling and analysis are critical for: the development and evaluation of Hg emission control technologies; use as Hg control technology process controls; and potential use as compliance tools. Research is specifically needed to:

- Develop and verify a manual test method that is suitable for measuring total and speciated Hg at sampling locations upstream of PM control devices,
- Develop and verify a manual test method that can simultaneously measure speciated Hg and other hazardous trace metals,
- Develop and demonstrate measurement techniques that are capable of directly identifying and quantifying trace levels of individual ionic species of Hg [e.g., HgCl₂, HgCl, HgO, HgS, HgSO₄, and Hg(NO₃)₂],
- Develop and demonstrate improved Hg CEM measurement techniques that address known and potential measurement obstacles (e.g., PM artifacts, interferences/biases, conversion systems, and sample conditioning/delivery),

- Verify the ability of Hg CEMs to accurately measure total gas-phase Hg and speciated gas-phase Hg at diverse stack conditions representative of fuel type and pollution control device configurations (e.g., downstream of PM control devices, dry FGD scrubbers, and wet FGD scrubbers),
- Verify the ability of Hg CEMs to accurately measure total gas-phase Hg and speciated gas-phase Hg upstream of PM control devices,
- Demonstrate Hg CEM long-term monitoring performance and operational requirements,
- Identify and evaluate CEMs capable of measuring SO₃ and other hazardous air pollutant emissions,
- Identify and evaluate alternative, cost-effective semi-continuous methods for measuring the stack emission of total Hg, and
- Demonstrate the use of Hg CEMs and semi-continuous monitoring methods as potential Hg emission compliance tools.

10.3 Mercury Speciation and Capture

10.3.1 Mercury Speciation

When the coal is burned in an electric utility boiler, the resulting high combustion temperatures vaporize the Hg in the coal to form gaseous elemental mercury (Hg⁰). Subsequent cooling of the combustion gases and interaction of the gaseous Hg⁰ with other combustion products result in a portion of the Hg being converted to gaseous oxidized forms of mercury (Hg²⁺) and particle-bound mercury (Hg_p). The term *speciation* is used to denote the relative amounts of these three forms of Hg in the flue gas of the boiler. It is important to understand how Hg speciates in the boiler flue gas because the overall effectiveness of different control strategies for capturing Hg often depends on the concentrations of the different forms of Hg species present in the boiler flue gas.

In general, Hg speciation is dependent on: 1) coal properties, 2) combustion conditions, 3) the flue gas composition, 4) fly ash properties, 5) the time/temperature profile between the boiler and air pollution control devices, and 6) the flue gas cleaning methods, if any, in use. The mechanisms by which Hg⁰ is oxidized in flue gas are believed to include gas-phase reactions, fly ash or deposit-mediated reactions, and oxidation reactions in post-combustion NO_x control systems. Data reveal that gas-phase oxidation is kinetically limited and occurs due to reactions of Hg with oxidizers such as Cl and Cl₂. Research also suggests that gas-phase oxidation may be inhibited by the presence of NO, SO₂, and water vapor.

Certain fly ashes have been shown to promote oxidation of Hg^0 more than others. The differences in oxidation appear to be attributable to the composition of the fly ash and the presence of certain flue gas constituents. The results of bench-scale research conducted at EPA indicate that the presence of HCl and NO_x in flue gas and iron in fly ash assists in oxidation. Other research indicates that $\gamma\text{-Fe}_2\text{O}_3$ may be causing Hg^{2+} formation and that surface area may be a dominant factor in this regard. Also, there are indications that HCl , NO_2 , and SO_2 in the flue gas may contribute to Hg^0 oxidation, while the presence of NO may suppress Hg^0 oxidation.

10.3.2 Development and Evaluation of Sorbents

Mercury can be captured and removed from a flue gas stream by injection of a sorbent into the exhaust stream with subsequent collection in a particulate matter (PM) control device such as an ESP or a FF. However, adsorptive capture of Hg from flue gas is a complex process that involves many variables. These include the temperature and composition of the flue gas, the concentration of Hg in the exhaust stream, and the physical and chemical characteristics of the sorbent (and associated functional groups). The implementation of an effective and efficient Hg control strategy using sorbent injection requires the development of low-cost and efficient Hg or multipollutant sorbents. Of the known Hg sorbents, activated carbons and calcium-based sorbents have been the most actively studied.

Oxidized mercury is readily absorbed by alkaline solutes/slurries or adsorbed by alkaline particulate matter (or by sorbents). Flue gas desulfurization systems, which use alkaline materials to neutralize the acidic SO_2 gas, remove Hg^{2+} effectively in the flue gas. Current research is focusing on optimization of the existing desulfurization systems as a retrofit technology for controlling Hg^{2+} emissions and on development of new multipollutant control technologies for simultaneously controlling both SO_2 and Hg emissions. Sorbents containing oxidizing agents are also being developed for the oxidation and capture of Hg^0 .

10.4 Evaluation of EPA ICR Mercury Emission Test Data

The air pollution control technologies used on coal-fired utility boilers exhibit levels of Hg control that range from 0 to 99 percent. The best levels of control are generally obtained by emission control systems that use FFs. Since Hg emission control technologies are not currently used by the utility industry, the capture of Hg by existing controls results from: 1) adsorption of Hg onto fly ash with subsequent capture of Hg_p in a PM control device; 2) adsorption of Hg by the alkaline sorbents used in dry scrubbers; or 3) the capture of Hg^{2+} in wet scrubbers.

The amount of Hg captured by a given control technology is better for bituminous coal than for either subbituminous coal or lignite. The lower levels of Hg capture in plants firing subbituminous coal and lignite are attributed to low fly ash carbon content, and the higher relative amounts of Hg^0 in the flue gas are due to the combustion of these fuels.

Combinations of coal, boiler, and control technologies that are expected to behave in a similar manner with respect to speciation and capture of mercury can be grouped into data sets

called coal-boiler-control technology classes. Accordingly, the ICR Part III emission data were sorted into appropriate coal-boiler-control classes. Next, the data in each class were evaluated for consistency, and the data between classes were evaluated based on the current understanding of speciation and capture of mercury. With few exceptions, the differences in data between the different classes were consistent with this understanding.

Plants that employ only post-combustion PM controls display Hg emission reductions ranging from 0 to 93 percent. The lower levels of control were observed for units with FFs. Decreasing levels of control were shown for units with ESPs, PM scrubbers, and mechanical collectors.

Units equipped with dry scrubbers (SDA/ESP or SDA/FF systems) exhibited average Hg captures ranging from 98 percent for units burning bituminous coals to 3 percent for units burning subbituminous coal. The poor Hg capture in units firing subbituminous coal is attributed to the predominance of Hg^0 in the flue gas from these units.

The capture of Hg in units equipped with wet FGD scrubbers is primarily dependent on the relative amount of Hg^{2+} in the inlet flue gas. Average Hg captures in wet FGD scrubbers ranged from 33 percent, for one PC-fired ESP + FGD unit burning subbituminous coal, to 96 percent in a PC-fired FF + FGD unit burning bituminous coal. The high Hg capture in the FF + FGD unit is attributed to the increased oxidization and capture of Hg in the FF.

The EPA ICR data base provides a massive amount of data that can be mined for additional information. However, the usefulness of these data is limited by the uncertainty of some of the measurements and/or the information that the data set does not contain. Some of the uses and limitations of the EPA ICR data are summarized below.

The EPA ICR data provide:

- Reasonable estimates of national and regional emissions for total Hg, Hg^0 , Hg^{2+} , and Hg_p . The data cannot be used to predict the total and speciated Hg emissions of individual coal-fired power plants.
- Data for testing hypotheses and models that predict speciation and capture of Hg in coal-fired boilers. The data cannot be used to identify or confirm specific mechanisms that control the speciation and capture of Hg.
- Information needed to guide the development of control technologies and identify effective strategies for the control of Hg emissions.

Caution should be used in interpreting the EPA ICR data since:

- Adsorption of Hg onto fly ash is highly dependent on fly ash properties, particularly on the fly ash carbon content. The lack of information on coal and fly ash properties greatly limits the usefulness of the ICR data.

- Results of Hg speciation measurements made with the OH Method upstream of PM control devices should be used with great caution. PM collected on the sampling train filter can result in physical and chemical transformations (e.g., sample artifacts) within the sample train.
- Because of the limited number of samples, there is a great deal of uncertainty in the central values and statistical characteristics of the ICR data. The flue gas Hg tests represent a short snapshot in time, and the effects of long-term variations in coal properties and plant operating conditions are unknown.
- At low inlet and outlet concentrations, the imprecision of the OH Method can obscure real differences between inlet and outlet concentrations.

10.5 Potential Retrofit Mercury Control Technologies

A practical approach to controlling Hg emissions at existing utility plants is to minimize capital costs by adapting or retrofitting the existing equipment to capture Hg. For units that currently use only PM controls, dry FGD scrubbers, or wet FGD scrubbers, there are three potential retrofit options: 1) Cold-side ESP, hot-side ESP, and FF systems; 2) Dry FGD systems; and 3) Wet FGD systems.

10.5.1 Cold-side ESP, Hot-side ESP, and FF Systems

The most cost-effective retrofit options for the control of Hg emissions from units, currently equipped with only an ESP or FF, include:

- Injection of a sorbent upstream of a cold-side ESP or FF. Cooling of the stack gas and/or modifications to the ducting may be needed to keep sorbent requirements at acceptable levels.
- Injection of a sorbent between a cold- or hot-side ESP and a pulsejet FF retrofitted downstream of the ESP. This approach will increase capital costs but reduce sorbent costs.
- Installation of a semi-dry CFA upstream of an existing cold-ESP used in conjunction with sorbent injection. The CFA recirculates both fly ash and sorbent to create an entrained bed with a high number of reaction sites. This leads to higher sorbent utilization and enhanced fly ash capture of Hg and other pollutants.

Units equipped with a FF require less sorbent than units equipped with an ESP. ESP systems depend on in-flight adsorption of Hg by entrained fly ash or sorbent particles. FFs obtain both in-flight and fixed-bed capture as the flue gas passes through the FF.

In general, cost-effective sorbent injection technologies for cold-side ESP units will depend on: (1) the development of lower cost and/or higher performing sorbents, and (2) appropriate modifications to the operating conditions or equipment being currently used to control emissions of PM, NO_x, and SO₂.

It is believed that the above technologies will be available for use on boiler units that must comply with the Clean Air Act hazardous air pollutant (HAP) maximum achievable control technology (MACT) requirements for electric utility steam-generating units. The performance and cost of these technologies are yet to be determined.

10.5.2 Semi-dry FGD scrubbers

Semi-dry FGD scrubbers are already equipped to control emissions of SO₂ and PM. The modification of these units by the use of appropriate sorbents for the capture of Hg and other air toxics is considered to be the easiest retrofit problem to solve. SDA/FF systems are capable of higher levels of Hg control than SDA/ESP systems.

10.5.3 Wet FGD Scrubbers

Improvements in wet FGD scrubber performance in capturing Hg depend primarily on the oxidation of Hg⁰ to Hg²⁺. This may be accomplished by 1) the injection of appropriate oxidizing agents, or 2) the installation of fixed oxidizing catalysts upstream of the scrubber to promote oxidation of Hg⁰ to soluble Hg compounds.

An alternative strategy for controlling Hg emissions from wet FGD scrubbing systems is to inject sorbents upstream of the PM control device. Better performance can be expected for units equipped with FFs than those equipped with ESPs. SCR systems used with wet FGD scrubbers may enhance Hg capture in the scrubber.

Additional research is needed on the oxidation of Hg⁰ and the removal and sequestration of Hg collected in the scrubbing liquid.

10.6 Costs of Retrofit Mercury Control Technologies

Preliminary annualized costs of Hg controls using powdered activated carbon (PAC) injection have been estimated based on recent pilot-scale evaluations with commercially available sorbents. These control costs range from 0.305 to 3.783 mill/kWh, with the highest costs associated with plants having hot-side electrostatic precipitators (HS-ESPs). For plants representing approximately 89 percent of current plant capacity and using controls other than HS-ESPs, the costs range from 0.305 to 1.915 mill/kWh. Assuming a 40 percent reduction in sorbent costs by use of a composite lime-PAC sorbent for Hg removal, cost projections range from 0.183 to 2.27 mill/kWh, with higher costs again being associated with the plants using HS-ESPs.

In comparison, the estimated annual costs of Hg controls, as a function of plant size, lie mostly between the costs for low-NO_x burners (LNBs) and selective catalytic reduction (SCR) systems. The costs of Hg control will dramatically diminish if retrofit hardware and sorbents are employed for control of other pollutants such as NO_x, SO₂, or fine PM.

The performance and cost estimates of PAC injection-based Hg control technologies presented in this report are based on relatively few data points from pilot-scale tests and are considered to be preliminary. However, based on data from pilot-scale tests and the results of ICR data evaluations, it is expected that better sorbents and technologies now being developed will reduce the costs of Hg controls beyond current estimates.

Within the next 2-3 years, it is expected that the evaluation of retrofit technologies at plants where co-control is being practiced will lead to a more thorough characterization of the performance and costs of Hg control. Future cost studies will focus on the development of performance and cost information needed to: 1) refine cost estimates for sorbent injection based controls, 2) develop cost estimates for wet scrubbing systems that employ methods for oxidizing Hg⁰, and 3) determine the costs of various multipollutant control options.

The issue of Hg in many power plant residues will also be examined to address concerns related to the release of captured Hg species into the environment. These evaluations will be conducted in conjunction with the development and evaluation of air pollution emission control technologies.

10.7 Coal Combustion Residues and Mercury Control

Power plant operations result in solid discharges including fly ash, bottom ash, boiler slag, and FGD residues. These residues already contain Hg, presumably bound Hg that is relatively insoluble and non-leachable. In 1998, approximately 108 million tons of coal combustion residues (CCRs) were generated. Of this amount, about 77 million tons were land-filled and about 31 million tons were utilized for beneficial uses.

Increased control of Hg emissions from coal-fired power plants may change the amount and composition of CCRs. Such changes may increase the potential for release of Hg to the environment from either land filling (approximately 70 percent) or commercial uses (approximately 30 percent) of CCRs. Mercury volatilization from CCRs in landfills and/or surface impoundments is expected to be low due to the low temperatures involved and minimal gas-to-solid interfaces within impacted wastes. For Hg control retrofits involving dry or wet FGD scrubbers, the residues are typically alkaline and the acid leaching potential of Hg from these residues is expected to be minimal.

There are several commercial uses of CCR where available data on which to characterize the Hg emission potential are lacking. The following CCR uses are given a priority for developing additional data in order to characterize the ultimate fate of Hg:

- Use of fly ash in cement production,

- Volatilization and leaching of residues used for structural fills,
- Leaching of residues exposed to acidic conditions during mining applications,
- Volatilization of Hg during the production of wallboard from gypsum in wet scrubber residues,
- Mercury volatilization during the production and application of asphalt with fly ash fillers, and
- Leaching or plant uptake of Hg from fly ash, bottom ash, and FGD sludge that are used as soil additives.

10.8 Current and Future Research

It is important to continue collaborative Hg research efforts between DOE, EPA, EPRI, and the utility industry. The focus of these efforts should be to provide scientific and engineering data that support the Administration's Energy Plan and that can be used to:

- Develop HAP MACT requirements for coal-fired electric utility steam generating units.
- Optimize control of Hg emissions from units that must comply with more stringent NO_x emission requirements under the NO_x state implementation plan (SIP) call.
- Develop technologies that can be used to control emissions under multipollutant control legislation that is under consideration by the Congress.

Current and future research is needed to:

- Control Hg emissions for units now equipped only with ESPs.
- Develop cost-effective sorbents to control emissions from subbituminous coals and lignite.
- Control Hg⁰ emissions from subbituminous coals and lignite.
- Determine the effects of coal blending on Hg speciation and capture.
- Evaluate the enhancement of fly-ash capture by combustion modification techniques.

- Develop Hg⁰ oxidizing methods for wet FGD systems.
- Optimize NO_x controls for Hg control.
- Evaluate controls for non-PC fired units.
- Control Hg, SO₃, and other air toxic emissions from units equipped with SCR and wet FGD scrubbers.
- Demonstrate Hg control for units with SD/ESP and SD/FF.
- Demonstrate Hg control in wet FGD systems.
- Determine the effects of cyclone, stoker, and fluidized-bed combustion systems on Hg control.
- Minimize the effects of Hg controls on power plant operability.
- Conduct tests with CEMs to study the variability of Hg emissions.
- Characterize and control the stability of Hg and other hazardous trace metals in CCRs and byproducts.